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CORRELATION ANALYSIS AS A TOOL TO INVESTIGATE THE BIOACCESSIBILITY OF NICKEL, VANADIUM AND ZINC IN NORTHERN IRELAND SOILS

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Abstract: Correlation analyses were conducted on nickel (Ni), vanadium (V) and zinc (Zn) oral bioaccessible fractions (BAFs) and selected geochemistry parameters to identify specific controls exerted over trace element bioaccessibility. BAFs were determined by previous research using the Unified BARGE Method. Total trace element concentrations and soil geochemical parameters were analysed as part of the Geological Survey of Northern Ireland Tellus Project. Correlation analysis included Ni, V and Zn BAFs against their total concentrations, pH, estimated soil organic carbon (SOC) and a further eight element oxides. BAF data were divided into three separate generic bedrock classifications of basalt, lithic arenite and mudstone prior to analysis, resulting in an increase in average correlation coefficients between BAFs and geochemical parameters. Sulphur trioxide and SOC, spatially correlated with upland peat soils, exhibited significant positive correlations with all BAFs in gastric and gastro-intestinal digestion phases, with such effects being strongest in the lithic arenite bedrock group. Significant negative relationships with bioaccessible Ni, V and Zn and their associated total concentrations were observed for the basalt group. Major element oxides were associated with reduced oral trace element bioaccessibility, with Al₂O₃ resulting in the highest number of significant negative correlations followed by Fe₂O₃. Spatial mapping showed that metal oxides were present at reduced levels in peat soils. The findings illustrate how specific geology and soil geochemistry exert controls over trace element bioaccessibility, with soil chemical factors having a stronger influence on BAF results than relative geogenic abundance. In general, higher Ni, V and Zn bioaccessibility is expected in peat soil types.

52 1. Introduction

53

54 Determining the bioaccessibility of potentially toxic elements in soil provides
55 supporting information to more accurately constrain human health risk assessment
56 approaches where oral soil borne contaminant exposure is the pathway of concern.
57 While much research has been conducted in terms of the bioavailability and
58 bioaccessibility of trace elements such as lead and arsenic, particularly from
59 anthropogenic sources (Farmer et al. 2011; Meunier et al. 2010; Palumbo-Roe and
60 Klinck 2007), a knowledge gap exists concerning the bioaccessibility of a wider
61 range of metals and metalloids from geogenic sources.

62

63 Previous research suggests that toxic elements from geogenic sources may be less
64 bioaccessible than those associated with anthropogenic contamination due to the
65 solid phases in which they exist (Cave et al. 2007; Cave et al. 2003). Such
66 findings have implications for human health risk assessments in the context of the
67 United Kingdom's (UK) contaminated land legislation regime (DEFRA 2012), as
68 better determination of specific health risks could avoid unnecessary soil
69 remediation projects. In addition, correlating trace element abundance and
70 bioaccessibility to specific soil types, geochemical parameters and parent bedrock
71 geology can identify natural controls exerted over the bioavailability of geogenic
72 contaminants, facilitating more accurate site-specific risk assessments.

73

74 In Northern Ireland, nickel (Ni), vanadium (V) and zinc (Zn), whose distributions
75 are largely controlled by local geology, are present in soils at elevated levels,
76 exceeding either Environment Agency (EA) Soil Guideline Values (SGVs) or
77 other existing available generic assessment criteria (Barsby et al. 2012; EA 2009a;
78 Nathanail et al. 2009). However, assessment criteria must be used with care, and
79 particular attention should be paid to the derivation of such guideline values. For
80 example, arsenic health criteria values and subsequent SGVs have been derived
81 using toxicology data from exposure to soluble forms of arsenic in drinking water
82 rather than from exposure via soil media (EA 2009b; EA 2009c). Where Ni is
83 concerned, the inhalation pathway is considered to be the most significant
84 exposure route capable of introducing human health risks, although toxicological
85 information suggests some forms of Ni are still readily absorbed through the

86 gastro-intestinal tract when ingested and, therefore, still capable of inducing toxic
87 health effects (EA 2009a; EA 2009d). Such challenges regarding the accurate
88 characterization of risks associated with soil-borne trace element exposure
89 highlight the need for employing more detailed assessment techniques such as
90 bioaccessibility testing, thus ensuring exposure pathways are relevant to specific
91 toxic effects, land use scenarios and contaminant sources.

92
93 In response to these issues, much research has been conducted over the past two
94 decades in order to refine a suitable methodology for bioaccessibility testing
95 where ingestion of soil is the exposure pathway of concern (Wragg et al. 2011;
96 Wragg et al. 2009; Wragg and Cave 2003; Van de Weile et al. 2007; Oomen et al.
97 2003; Ruby et al. 1999; Ruby et al. 1996). The most recently published
98 methodology widely in use in the UK and European Union to date, the Unified
99 BARGE (BioAccessibility Research Group of Europe) Method (UBM), has been
100 validated against *in vivo* data for arsenic, cadmium and lead (Denys et al. 2012;
101 BARGE/INERIS 2010; Caboche 2009). A recently published study by Barsby et
102 al. (2012) was the first bioaccessibility investigation of its kind covering the
103 region of Northern Ireland and employing the UBM. The findings of this study
104 suggested that trace element bioaccessibility was specific to individual geologic
105 formations within the region, thus unveiling a wider scope of investigation for
106 determining in more detail the mechanisms governing this variability.

107
108 Specific soil properties such as redox potential, parent rock material, organic
109 content, pH, nutrient content, and the co-occurrence of major element oxides can
110 influence the mobility and bioavailability of toxic elements in soil. For example,
111 Poggio et al. (2009) found soil organic matter was positively correlated with the
112 bioaccessibility of several trace metals, including Ni and Zn. Where Zn is
113 concerned, decreased bioaccessibility has been associated with the presence of
114 aluminium oxides, and its mobility and resulting bioaccessibility may also be
115 affected by the presence of organic matter (Pelfrène et al. 2012; Nathanial et al.
116 2009; Poggio et al. 2009; ATSDR 2005). Less information is available to date
117 concerning such relationships for V, although acidic pH has been found to reduce
118 its mobility in soil (Nathanail et al. 2009), which is in contrast to other trace
119 metals where solubility generally increases under acid soil conditions. Chemical

120 conditions that are conducive to increased element mobility and solubility will in
121 turn enhance bioaccessibility.

122

123 The aim of this paper is to illustrate how geology and geochemistry influence
124 trace element bioaccessibility by using correlation analyses to identify
125 relationships between Ni, V and Zn bioaccessible fractions (BAFs) in soil and
126 selected geochemistry variables. With Northern Ireland's diverse geology,
127 unsurpassed by any other country of a similar size (Jordan et al. 2007; Mitchell
128 2004; Wilson 1972), such a study has wider applications beyond the immediate
129 study area when conducting site-specific human health risk assessments.

130

131 2. Methodology

132

133 2.1 Study Area

134

135 The range of bedrock types encountered in Northern Ireland forms a stratigraphic
136 record which commences in the Mesoproterozoic era, comprising deformed and
137 metamorphosed sedimentary and volcanic rocks formed at least 600 million years
138 ago (Mitchell 2004). The region includes examples of all geological systems up
139 to and including the Palaeogene period, comprising basalt lavas and lacustrine
140 sedimentary rocks formed between circa 55 and 62 million years ago. Quaternary
141 processes involved the advance of ice sheets and their meltwaters, resulting in a
142 range of diverse superficial deposits including glacial till. As a result, superficial
143 deposits such as glacial till and post-glacial alluvium cover at least 80% of
144 bedrock in the region. The rock types encountered find stratigraphic distribution
145 beyond Northern Ireland and, thus, findings in relation to pedological and
146 geological controls on trace element bioaccessibility associated with specific soil
147 and rock geochemical signatures has applications beyond the immediate region of
148 Northern Ireland.

149

150 Data associated with sample locations presented for this study are divided into
151 three generic bedrock types: basalt, lithic arenite and mudstone (Fig. 1). The
152 rationale for selection of these groups is provided in Section 2.4. The basalt lavas
153 of the Antrim Plateau are located in the northeast of the study region, with lithic

154 arenite sample locations occurring predominantly in the southeast in the County
155 Down area. In the southwest region of Fermanagh, sedimentary rock types are
156 present, classified generally as mudstones.

157

158 2.2 Geochemistry Analyses

159

160 The GSNI (Geological Survey of Northern Ireland) Tellus Survey, conducted
161 between 2004 and 2007, consisted of a comprehensive survey of stream sediments
162 and stream waters, as well as rural and urban soils. Composite rural soil samples
163 used for this research were collected from a total of 6,862 locations on a 2 km²
164 grid from a depth of 5-20 cm below ground level (Smyth 2007).

165

166 Soil geochemistry data relating to trace elements, element oxides and other
167 geochemical parameters including pH and loss on ignition (LOI; %) were
168 determined as detailed in the Tellus geochemical mapping methodology report
169 (Smyth 2007). Pseudo-total and total concentrations of Ni, V and Zn (mg kg⁻¹)
170 were determined both by *aqua regia* digestion followed by inductively coupled
171 plasma spectrometry (ICP), as well as by pressed pellet X-ray fluorescence
172 spectrometry (XRF). Major element oxides (%) were determined also by XRF.

173

174 LOI, applied as an estimate of soil organic carbon (SOC), was determined by
175 calculating sample weight loss after oven drying at 105°C for 4 hours followed by
176 4 hours in a 450°C furnace. While not a means of determining the precise carbon
177 content of soils, the LOI method is recognised as a suitable, cost-effective
178 approach to estimating regional trends in SOC and has been applied in other
179 published research (Salehi et al. 2011; Elzinga and Cirimo 2010; Konen et al.
180 2002; Ball 1964).

181

182 2.3 Unified BARGE Method Testing

183

184 The UBM is a sequential extraction technique designed to mimic the conditions of
185 the human digestive system. Three stages of the UBM aim to represent the
186 salivary, stomach and intestinal exposure conditions of an ingested material. Two
187 extracts are collected from the method: one following a one hour gastric digestion

188 using synthesised saliva and stomach fluids, and a second extract is obtained after
 189 an additional four hours of gastro-intestinal digestion using synthesised duodenal
 190 fluid and bile. Details of the UBM protocol and required equipment and reagents
 191 are available on the BARGE web site (BARGE/INERIS 2010). UBM laboratory
 192 work was carried out at the British Geological Survey (BGS) in Keyworth,
 193 Nottingham. Methodology and quality control efforts used to obtain the
 194 bioaccessibility data referred to in this paper have been published previously
 195 (Barsby et al. 2012). For every 10 samples analysed by the UBM, one duplicate,
 196 one blank and one reference soil (BGS 102; Wragg et al. 2009) were extracted.

197

198 As described in Barsby et al. (2012), the trace element oral bioaccessibility was
 199 determined on a subset of archived surface soil samples from the original rural
 200 soil sampling programme of the GSNI Tellus Survey. Soil samples used for UBM
 201 testing, comprising 91 samples in total, were chosen with the aim of representing
 202 a broad spatial, lithological and pedological coverage across the region. Dried
 203 and sieved soil from the <250µm fraction was used for the UBM digestion.

204

205 Bioaccessible trace element concentrations were measured by inductively coupled
 206 plasma mass spectrometry (ICP-MS) following gastric (G) and the gastro-
 207 intestinal (GI) UBM extraction. BAFs (%) were calculated using bioaccessible
 208 concentrations determined from the UBM test (C_b) and the total XRF
 209 concentration in the soil sample as provided by the Tellus Survey data base (C_{pt}).

210

$$BAF [\%] = \frac{C_b[mg\ kg^{-1}]}{C_{pt}[mg\ kg^{-1}]} \times 100$$

211

212 (Equation 1).

213

214 XRF total concentrations were chosen for BAF calculation instead of ICP pseudo-
 215 total concentrations because of the ability of XRF analysis to detect insoluble
 216 traces of elements, providing a better understanding of total trace element
 217 bioaccessibility in terms of insoluble, geogenic mineral forms. Relative BAF
 218 results (%) were used for the correlation analyses as opposed to absolute UBM

219 extract concentration values to provide a normalised basis for comparison of
220 relative trace element bioaccessibility across geologic sub-groups.

221

222 2.4 Statistical Treatment and Grouping of Data

223

224 Correlation analyses were carried out using G- and GI-BAFs of the three trace
225 elements against the following geochemical variables: oxides of magnesium
226 (MgO), aluminium (Al₂O₃), silicone (SiO₂), sulphur (SO₃), phosphorous (P₂O₅),
227 calcium (CaO), manganese (MnO), and iron (Fe₂O₃); total Ni, V and Zn
228 concentrations; SOC; and pH. A two-tailed significance test was applied using
229 the Pearson's correlation coefficient (*r*) in IBM SPSS Statistics v.19. Cut off
230 points for critical *r* values were determined according to sample group sizes as
231 defined in Triola (1998).

232

233 Initial exploration of distribution trends in the Tellus geochemistry data set
234 indicated that, while all geochemistry data were not normally distributed when
235 tested for skewness and kurtosis, log-transformation of the data did not
236 substantially improve tendencies towards normal distributions. When Tellus
237 geochemistry data were divided into geologic sub-groups, the tendency towards a
238 normal distribution was increased. Parametric statistical testing was therefore
239 deemed suitable for the purpose of these analyses.

240

241 Correlation analyses were first conducted on the complete bioaccessibility study
242 set (*n* = 91). This sample set was subsequently divided into geologic sub-groups
243 according to three generic bedrock types present in the study set in the highest
244 proportions as defined by the GSNI Tellus Survey methodology (Smyth 2007).
245 This was carried out with the aim of controlling for geogenic influences in the
246 geochemistry data and reducing potential sources of variance which could be
247 introduced from other soil properties or multiple rock types (Jordan et al. 2007;
248 Zhang et al. 2007). In turn, it was anticipated that the likelihood of identifying
249 geogenic controls over the BAF results would increase and correlation findings
250 would be strengthened.

251

252 The rationale for using generic bedrock types as defined in the GSNI Tellus
253 Survey rather than specific local formations was to ensure statistical robustness
254 was maintained through the formation of sufficient sub-group sample sizes. The
255 three generic bedrock types present in the bioaccessibility study set in the highest
256 proportions were identified as basalt ($n = 23$), consisting of Upper and Lower
257 Basalt formations, the Tardree Rhyolite Complex, the Causeway Tholeiite
258 Member, and the Slieve Gullion Complex; lithic arenite ($n = 17$), inclusive of
259 Gilnahirk, Gala and Hawick Sandstones; and the mudstone group ($n = 18$),
260 represented by a mixture of sedimentary bedrock types including clays,
261 limestones, mudstones and shales.

262

263 2.5 Spatial Data Analysis

264

265 Spatial interpolation by inverse distance weighting (IDW) was applied to the
266 Tellus XRF geochemistry data set to illustrate geographic patterns in specific
267 spatial variables of interest. Mapped outputs of total toxic trace element
268 concentrations are presented in Barsby et al. (2012). IDW is a deterministic
269 method, resulting in a clustering of values around data points on the surface
270 through exact interpolation (Lloyd 2010). This effect is reduced in regularly
271 gridded data such as the Tellus data used for this study. The IDW method
272 assumes that sample points further away spatially will have a diminished
273 influence over the interpolated value at a given location, while points closer to a
274 specific location will have a greater influence over its predicted value (ESRI
275 2010; Matheron 1965).

276

277 ArcGIS v.10 was used to map the spatial distribution of selected geochemical
278 variables from the complete Tellus geochemistry database ($n = 6862$) using IDW
279 with a power function of 2, a variable search radius and an output cell size of 250.
280 An iterative process was used to select the best fit model from four different
281 possible single-sector search neighbourhoods of 8, 10, 12 or 15 neighbours. The
282 function resulting in the best fit regression model of prediction was chosen based
283 on values of mean prediction error, root mean square error and the slope of the
284 regression function.

285

286 3. Results

287

288 When average BAF results were compared across the three generic bedrock types,
289 differences in relative trace element bioaccessibility were observed (Table 1).
290 The highest measured mean and maximum G-BAF for V was in the basalt group.
291 However, the mean GI-BAF was greatest in the mudstone group. Zn G-BAF
292 averages were also higher in soil samples located over basalt bedrock types, while
293 differences in mean GI-BAFs were negligible, with the exception of the lithic
294 arenite bedrock group where the lowest Zn GI-BAF was observed. Both mean G-
295 and GI-BAF results for Ni were highest in the mudstone bedrock group, although
296 the maximum G- and GI-BAFs occurred in soil samples collected over basalt and
297 lithic arenite, respectively. The basalt group also displayed minimum G- and GI-
298 BAFs where Ni was concerned.

299

300 Table 2 provides a summary of Pearson's correlation coefficients (r) for selected
301 geochemical parameters and UBM BAF data. In general, total trace element
302 concentrations were associated with reduced BAFs in the basalt sample group.
303 The same trend was apparent for MgO, MnO, P₂O₅ and Fe₂O₃ within this bedrock
304 group, with P₂O₅ revealing significant negative correlations to Ni, V and Zn BAFs
305 in the basalt samples only. Al₂O₃ showed strong negative influences over all trace
306 element BAFs, particularly for the basalt and mudstone samples. The effect of
307 silicates expressed in the form of SiO₂ was less pronounced in terms of number of
308 significant correlations; however, where this oxide was significantly correlated
309 with Ni, V and Zn BAFs, it appeared to exert a negative control over
310 bioaccessibility primarily in the gastric digestion phase. While SO₃ and SOC
311 were consistently positively correlated with gastric BAFs, their effects were
312 strongest across both digestion phases in the lithic arenite bedrock group.

313

314 3.1 Vanadium

315

316 When V BAF results were analysed for correlations with other geochemical
317 properties within the bioaccessibility study sample set, significant negative
318 correlations were found between gastric BAFs and MgO, Al₂O₃, SiO₂, MnO, and
319 Fe₂O₃ ($p \leq 0.01$). Positive G-BAF relationships were observed with SO₃ and

320 SOC, also at the 0.01 significance level. Different effects on V BAFs were
321 apparent in the correlation data when gastro-intestinal BAFs were analysed. GI-
322 BAFs decreased in line with increasing total V and Ni content. MgO, MnO,
323 Fe₂O₃ and Al₂O₃ continued to exert negative effects over V BAFs in the gastro-
324 intestinal digestion phase, although the trend with SiO₂ observed in the gastric
325 digestion phase was weakened to a point of non-significance. SO₃ and SOC
326 exhibited a significant positive relationship with V GI-BAFs ($p \leq 0.01$), although
327 Pearson's correlation coefficients were reduced when compared to the G-BAF
328 data.

329

330 When BAFs were split into specific Tellus geology classifications, a number of
331 previously observed correlations changed. Average absolute r values for G-BAFs
332 against geochemical parameters were 0.58, 0.35 and 0.38 for the basalt, lithic
333 arenite and mudstone groups, respectively, compared to an average correlation
334 coefficient of 0.31 when correlations were conducted on the complete study set.
335 Average absolute r values for GI-BAF correlations doubled in the basalt group,
336 increased by 0.10 in the lithic arenite bedrock group, and improved by 0.16 in the
337 mudstone bedrock group when compared to statistics obtained from the full study
338 set prior to bedrock group division.

339

340 Overall, the greatest number of significant correlations between bioaccessible V
341 and geochemistry variables was observed in the basalt bedrock group. Both G-
342 and GI-BAFs were negatively correlated with total V, Ni and Zn ($p \leq 0.05$).
343 MgO, Al₂O₃, P₂O₅, MnO and Fe₂O₃ also showed strong significant negative
344 correlations with bioaccessible V in the gastric and gastro-intestinal phases (-0.55
345 $\geq r \geq -0.77$; $p \leq 0.01$). Increasing soil acidity appeared to result in increased V
346 bioaccessibility according to G- and GI-BAF correlation values. SO₃ and SOC
347 exerted the strongest positive influence over gastric bioaccessible V, although no
348 significant r values were obtained for these variables within the basalt GI data.

349

350 The strongest negative correlations in soil samples overlying lithic arenite bedrock
351 were observed with Al₂O₃ and Fe₂O₃, while the highest positive correlations were
352 found with SO₃ and SOC. SiO₂ also appeared to have a negative effect over G-
353 and GI-BAFs, though correlations were statistically significant in the gastric data

354 only ($p \leq 0.05$). Correlations in this bedrock group did not vary substantially
355 when gastric and gastro-intestinal digestion phases were compared.

356

357 In the mudstone bedrock group, MgO, Al₂O₃ and MnO showed consistent
358 negative correlations with V BAFs in both the G and GI digestion phases.
359 Significant correlations were observed for Fe₂O₃ and pH in the GI-BAF data only.
360 In contrast to the inverse correlation observed between pH and BAFs in the basalt
361 bedrock group, positive correlation statistics were obtained across these variables
362 in the mudstone group.

363

364 3.2 Nickel

365

366 As shown in Table 2, bioaccessible Ni decreased in line with increasing total V
367 and Ni, while the opposite was observed with total Zn. Within the complete study
368 set, similar relationships were observed between Ni BAFs and oxides of Mg, Al,
369 Mn and Fe, as were found in the V BAF data, with decreased levels of Ni
370 bioaccessibility associated with their occurrence. In addition to this trend, SO₃
371 and SOC continued to exert a positive influence over Ni G- and GI-BAF results,
372 with the largest r values obtained for the gastric BAF data.

373

374 In the basalt group, the average Pearson's correlation coefficient was 0.68 and
375 0.57 for the G- and GI-BAF data, respectively. Variables not producing
376 significant correlations in this group were SiO₂, SO₃ and SOC, though this lack of
377 influence was observed within the gastro-intestinal data only. Total Ni, V and Zn
378 were inversely correlated to Ni BAFs ($p \leq 0.01$) in the basalt samples, while no
379 such significant relationships were found in the other two bedrock classes.

380

381 Although the number of significant correlations in the lithic arenite group
382 decreased when compared to the full study set results, average correlation
383 coefficients still increased slightly for both gastric and gastro-intestinal Ni BAFs.
384 This suggests the capability to identify correlations as significant was restricted
385 due to the reduced sub-sample size rather than being a result of weakened absolute
386 r values. Most notably in the lithic arenite group, SO₃ and SOC showed strong

387 positive correlations with G-BAF data ($r = 0.94$ and 0.81 , respectively), and also
388 with GI-BAF results ($r = 0.89$ and 0.65 , respectively; all $p \leq 0.01$).

389

390 The trends with sulphur trioxide and estimated organic content continued in the
391 mudstone group, while oxides of aluminium and silica appeared to result in
392 significantly reduced Ni bioaccessibility in the G-BAF data. The impact of Al_2O_3
393 was still significant in the GI digestion phase ($p \leq 0.05$), though this effect was
394 reduced when compared to the G-BAF results. CaO was significantly correlated
395 with Ni G-BAFs, with bioaccessibility appearing to increase in line with CaO
396 concentrations. This impact was not consistent across the geologic formations,
397 however, with significant negative correlations observed for this variable in the
398 basalt bedrock group.

399

400 3.3 Zinc

401

402 Overall, Zn exhibited the highest mean and maximum G- and GI-BAFs compared
403 to Ni and V, with up to a quarter of total Zn found to be potentially bioaccessible
404 on average, reaching a maximum of 80% in the basalt group (Table 1). Following
405 a similar pattern to V and Ni, oxides of Mg, Al, Mn and Fe were negatively
406 correlated to Zn BAFs in both the G and GI fractions. Total V and Ni were also
407 negatively correlated with bioaccessible Zn in the full study set; however, there
408 was a weak relationship between total and bioaccessible Zn. SO_3 and SOC
409 exhibited the strongest positive correlations with Zn G-BAFs, though significant
410 correlation coefficients were still obtained across the GI-BAF data (maximum $r =$
411 0.95). pH was negatively correlated with Zn BAFs in the complete study set, and
412 this relationship was more clearly displayed within the basalt bedrock group.
413 However, this correlation was not significant in the other two bedrock groups ($p \geq$
414 0.05).

415

416 In the basalt bedrock category, the only parameter not yielding a significant
417 correlation with Zn BAFs was SiO_2 in the gastro-intestinal phase. The number of
418 significant correlations was substantially reduced in the other two bedrock groups
419 by comparison, although correlations with SOC, SO_3 , Fe_2O_3 and Al_2O_3 remained
420 strong overall. Additional significant negative correlations were observed

between total V, total Ni and Zn GI-BAFs in both the lithic arenite and mudstone groups ($p \leq 0.05$). SiO_2 was associated with decreased gastric Zn bioaccessibility across all sample sets, while P_2O_5 and CaO appeared to exert strong negative effects over G- and GI-BAFs in the basalt group. In contrast, P_2O_5 and CaO yielded weakly positive r values in the mudstone bedrock group, although statistical significance was limited to CaO and the gastric bioaccessible fraction ($r = 0.76, p \leq 0.01$).

3.4 Spatial Trends

As shown by the correlation analysis (Table 2), SO_3 and SOC consistently exerted positive controls over the bioaccessibility of the three trace elements. In addition, SO_3 and SOC are strongly correlated to each other across Northern Ireland ($r = 0.86, p \leq 0.01$). As shown by Fig. 2c and d, SO_3 and SOC share similar spatial distributions across Northern Ireland, overlapping directly with the extent of acid upland peat soils. Overall, the range of pH values in Northern Ireland soils is relatively narrow (Fig. 2a), making definite correlations with BAF data difficult to distinguish in the absence of a wider range of pH values. Although soil pH did not appear as a factor affecting bioaccessibility as significantly as SOC and SO_3 through the correlation analysis, more acidic soil conditions are shown to be well-aligned spatially with peat soils in the region. In addition, spatial illustration of the distribution of aluminium oxide (Fig. 2b), which exerted consistent negative controls over Ni, V and Zn BAFs, shows lower relative abundances in peaty upland areas, with additional strong geologic controls over Al oxide distribution around the Antrim Basalts in the northeast of the country. Interpolation of other metal oxides associated with reduced BAFs such as Fe_2O_3 (not shown) resulted in similar spatial distributions to Al_2O_3 .

4. Discussion

4.1 Geogenic Sources of Variance

Correlation analysis is a useful tool for identifying relationships between pairs of variables and for forming hypotheses on element sources, fate and behaviour.

Such analyses can also support the development of mathematical models to predict trace element bioaccessibility under certain conditions (Pelfrène et al. 2012; Abollino et al. 2011; Poggio et al. 2009; Cave et al. 2007; Cave et al. 2003). It is important to note, however, that correlation does not necessarily imply causation (Triola 1998), and some of the geochemistry variables explored in this study may be mere micro-scale indicators of wider scale factors or processes bearing influence over trace element bioaccessibility. For example, some of the oxides studied are used as indicators of rock and mineral weathering processes which may be responsible for mobilising trace elements across large regional scales.

While correlation analysis can assist with understanding specific mechanisms that may influence trace element bioaccessibility, potential geogenic sources of variance in geochemistry data should be eliminated before these relationships can be effectively explored, particularly in Northern Ireland where such diversity in geology exists (Jordan et al. 2007). The increase in average correlation coefficients when the UBM data were split into the three dominant generic bedrock types indicates that variability was reduced within the geologic subgroups. However, other sources of variability capable of weakening correlation statistics are still present within these data sets. Soil type, for example, is a variable that was not initially controlled for within the bedrock groups, although it is a variable that was revealed during the course of analysis, in the case of peat. At least eight distinctly different soil types are present within each of the basalt and mudstone sample groups, while shale soil types dominated in the lithic arenite division. Despite the variety of soil types in the basalt group, the high Pearson's correlation coefficients for most parameters suggests that a large source of variance in BAF data stems from geology in this area. Lower r values in the other bedrock groups suggest significant sources of variance are present in the results not accounted for by bedrock type. For example, soil type or localised physico-chemical factors such as soil moisture or redox conditions could also influence trace element mobility and bioaccessibility.

Differences in relative trace element bioaccessibility between the generic bedrock groups (Table 1) may be attributed to Ni, V or Zn existing in different solid

489 phases over each bedrock type. For example, strong negative correlations
490 between trace element BAFs and their total concentrations in the basalt bedrock
491 group suggest most of the non-bioaccessible fraction of these elements is in an
492 insoluble form in these soils, with a lesser soluble component accounting for the
493 bioaccessible portion. This may be linked to the relative age of the basalt
494 formations, which are among the youngest and least weathered rocks in Northern
495 Ireland (Mitchell 2004). This conclusion is also supported by Cox et al. (2013),
496 whose analysis of the solid phase distributions of Ni from the same study area
497 found that soil samples containing greater proportions of Ni present in carbonate
498 phases also hosted more bioaccessible Ni. Conversely, soil samples containing
499 higher proportions of Ni hosted by Fe-oxides and clay had relatively lower Ni
500 bioaccessibility. Previous comparison of ICP-derived trace element
501 concentrations against XRF data for the same elements suggests that the relative
502 solubilities of trace elements are influential in determining trace element
503 bioaccessibility, with XRF concentrations commonly higher than ICP data due to
504 the application of solvent-based *aqua regia* extraction versus the dry pellet
505 analytical technique used for the XRF analyses (Barsby et al. 2012). Weaker
506 negative correlations observed between BAFs and total trace element
507 concentrations in the mudstone and lithic arenite bedrock groups may be related to
508 their overall lack of relative abundance within these areas, illustrated previously
509 by Barsby et al. (2012). The exception to this trend is illustrated by Zn BAFs,
510 which were higher on average than the other two elements studied. Compared to
511 Ni and V, Zn total distributions are controlled by a wider variety of rock types
512 other than basalt, with high relative concentrations also found in soils over
513 sandstone and limestone in the region.

514

515 While the overall trend in correlations with pH was weakly negative with respect
516 to trace element BAF data (Table 2), the mudstone group provided a consistent
517 exception to this result. A closer look at rock sub-types within this category
518 shows a mixture of limestone, clay, argillaceous rock and mudstone. The
519 presence of limestone in particular may have introduced variable results in the
520 laboratory due to the release of calcium carbonate into solution, creating unstable
521 pH conditions during *in vitro* UBM extractions. CaO also showed a similar trend
522 to pH with respect to its variable influence over trace element BAFs, depending

on how the data set was treated across the geologic classifications. Individual trends in CaO correlations were aligned with pH trends within the basalt and mudstone sample groups. Across Northern Ireland, CaO shows a significant positive correlation with pH ($r = 0.436$, $p \leq 0.01$). With respect to BAF correlation results, CaO and pH were both negatively correlated with BAFs in the basalt group, but positively correlated with BAFs in the mudstone group. Both basalt and limestone, included in the mudstone group, contribute to increased levels of calcium in Northern Ireland soils (Jordan et al. 2001). However, geogenic calcium in the basalt sample group may be in a less soluble form than calcium found in limestone parent material. Chesworth et al. (1981) found that the greatest proportion of calcium in basalt in Belbex, France was hosted by pyroxene and plagioclase minerals which were the least susceptible to degradation by weathering compared to other basalt minerals studied. This aligns with the finding by Cox et al. (2013), whose XRD analysis of basalt mineralogy in County Antrim, Northern Ireland confirmed the presence of the same weather and acid resistant, calcium-rich minerals. Conversely, trace metals associated with high carbonate soil components derived from calcium-rich parent material such as limestone are easily extracted when exposed to acid conditions, resulting in increased gastric bioaccessibility (Denys et al. 2007; Ljung et al. 2007; Nathanail et al. 2007; Cave and Wragg 1997). Despite the common acceptance that pH is largely influential over trace element bioaccessibility and mobility in the environment, demonstrating such a mechanism through the statistical methods applied here is difficult due to the highly controlled pH environment of UBM laboratory methods (Pelfrène et al. 2012; BARGE/INERIS 2010).

The relative abundances of co-occurring metal oxides were also associated with increased variability in BAF results between the three groups, in particular where Al, Mg, Mn and Fe oxides are concerned. Al_2O_3 showed strong negative influences over all trace element BAFs, particularly for the basalt and mudstone samples. As shown by Fig. 2b, higher proportions of aluminium oxide in soil are spatially correlated with basalt bedrock in the northeast of the region. Additionally, aluminium compounds are expected to be higher in soils associated with mudstone bedrock due to the clay content of soils from these parent materials (Sparks 1995; Theng 1974). While the negative correlations found with

aluminium oxide and Ni, V and Zn BAFs in this study may be due to geogenic or pedological co-occurrence, aluminium, iron, manganese and other metal oxides also participate in sorption and co-precipitation reactions capable of immobilising heavy metal cations in soils (Pelfrène et al. 2012; Laveuf et al. 2009; Cances et al. 2008; Cave et al. 2007; Ma et al. 2007; ATSDR 2005; Flynn et al. 2003; Ruby et al. 1999). In addition to chemically stabilising ionic forms of trace elements in soils, the presence of co-occurring metals and their associated oxides may provide an indication that trace elements are bound in insoluble solid phases of geogenic origin (Wragg et al. 2007; Jordan et al. 2001; Ruby et al. 1999). When studying the effects of weathering on element mobility in basalt, Chesworth et al. (1981) found that Al and Fe weathering products precipitated into crystalline mineral forms immediately after release from parent rock. In a study on the weathering products of basalt in South China, Ma et al. (2007) concluded that Al and Fe oxides and trace elements were mobilised during the weathering process, but subsequently were removed deeper in the soil profile through the formation of insoluble co-precipitates capable of encapsulating and storing trace elements. Considering that soluble forms of trace metals are more bioaccessible than insoluble ones, this supports the trend found in this study of reduced bioaccessibility in the presence of Al_2O_3 and Fe_2O_3 . However, more detailed information is required about the precise mineral forms in which these oxides and trace elements exist.

578

579 4.2 Soil-Chemical Influences

580

Beyond geogenic controls over trace element bioaccessibility, which are important within wide spatial and time scales, more dynamic micro-scale chemical processes should also be regarded as highly influential. Soil chemistry including pH, organic content, microbial processes, redox potential and cation exchange capacity will significantly affect trace element bioaccessibility on variable spatial and time scales, regardless of total element concentrations (Abollino et al. 2011; Finžgar et al. 2007; Ljung et al. 2007; Hursthouse 2001). The time scales over which these factors can influence bioaccessibility are variable, with half-life sorption of metals onto humic materials in peat occurring within a time scale as short as 5 seconds (Sparks 1995). Seasonal variations in

591 soil moisture and resulting redox changes can also affect trace element
592 bioaccessibility and mobility, exemplifying the dynamic factors of influence that
593 occur outside of geologic time and spatial scales.

594

595 One of the most consistent positive influences identified over trace element
596 bioaccessibility was estimated soil carbon content. Poggio et al. (2009) found
597 similar positive correlations between oral bioaccessible Ni and Zn and soil
598 organic matter, and Nathanail et al. (2009) cite soil organic content as a key
599 consideration when assessing risks to human health from soil-borne contaminant
600 exposure. In contrast to these and previous findings, Pelfrène et al. (2012)
601 concluded that SOC had a negative impact over gastric Zn bioaccessibility.
602 Despite this, the *absence* of organic matter deeper in the soil profile encourages
603 Al and Fe to form insoluble co-precipitates with trace elements, while organic
604 compounds present at the soil surface may form organic colloids that increase
605 element mobility (Ma et al. 2007). Aluminium in particular freely moves from A
606 to B soil horizons in acidic podzol soil types that are rich in organic humic
607 material (Chesworth et al. 1981). Although the exact mechanisms by which SOC
608 increases element bioaccessibility cannot be determined from this study, it is
609 apparent that the presence of organic matter supports environmental conditions
610 that are conducive to higher levels of oral trace element bioaccessibility.

611

612 While the presence of higher amounts of soil carbon is positively correlated with
613 oral bioaccessibility results in this study, the effects of carbon in the human GI
614 tract may be contrary to the *in vitro* trend. Ruby et al. (1999) suggest that the
615 presence of organic matter in the form of food or soil particles in the GI tract may
616 hinder trace element transport across the intestinal epithelium, effectively
617 reducing trace element bioavailability. Further to this, organic matter has also
618 been found to influence trace element speciation in the stomach phase of UBM
619 digestion, which may in turn influence the final toxicity of an element after
620 ingestion (Broadway et al. 2010). Ljung et al. (2007) also point out that soluble
621 metals may be released from other compounds in the stomach acid, but that higher
622 pH conditions in the intestine may cause insoluble precipitates to form, reducing
623 bioavailability prior to intestinal absorption. This observation may help explain
624 why correlation results for BAFs with SO_3 and SOC were stronger in the stomach

625 phase of digestion than the in the intestinal phase. It is also anticipated that
626 organic matter would be degraded to a high degree in the stomach acids,
627 potentially reducing the effects of this variable once digestate reaches the
628 intestinal phase.

629

630 Individual trace element chemistry and resulting behaviour in the environment
631 should also be considered where element mobility and bioaccessibility is
632 concerned. For example, higher Zn bioaccessibility when compared to Ni and V
633 may be associated with the tendency of Zn to commonly occur as a free ion in
634 natural systems (ATSDR 2005; CCME 1999). In a study of a suite of toxic metals
635 in soils, Poggio et al. (2009) also found that Zn bioaccessibility was higher when
636 compared to other metals studied. In nature, free Zn ions occur as Zn^{2+} which
637 readily participate in sorption reactions with negatively charged soil particles, Fe
638 and Mn oxides, clay minerals and organic matter. Low pH conditions discourage
639 such sorption mechanisms from taking place, while Zn precipitates will form
640 under alkaline conditions (Nathanail et al. 2009; ATSDR 2005; CCME 1999).
641 Although ionic sorption reactions have the ability to immobilise trace elements in
642 natural soil systems, such bonding mechanisms at the soil solution-particle
643 interface are driven by relatively weak forces. As a result, these bonds may be
644 easily broken by the acid conditions present in the human digestive system, re-
645 mobilising ions for GI uptake.

646

647 Correlations between sulphur and carbon content in Northern Ireland soils have
648 been explored previously by Jordan et al. (2001), where the narrow range of soil
649 pH in the region was also observed. Peat soils possess many of the chemical
650 characteristics frequently associated with elevated trace element bioaccessibility.
651 Acidic and water-logged, reducing conditions erode soil parent material,
652 mobilising trace and major elements into soluble ionic forms (Elzinga and Cirimo
653 2010; Imrie et al. 2008; Finžgar, 2007). Some elements may then either be
654 leached out of the soil as a result, or retained by the high abundance of negatively
655 charged organic matter (CCME 1999; Guo et al. 1997). If this mobilising effect
656 causes major elements to be solubilised and subsequently leached, this renders
657 them unavailable for participation in sorption reactions with trace elements, which
658 may be the case where low abundance of metal oxides was observed in acid soils

659 (Fig. 2). Further to this, the absence of oxygen under reducing conditions may
660 prevent the formation of metal oxides which require oxidative conditions (Wragg
661 et al. 2007). Another mechanism for decreased major element oxide
662 concentrations in water logged soils involves the biological and chemical
663 reduction of these oxides into insoluble sulphuric and organic precipitates (Guo et
664 al. 1997), where elements are effectively removed from soil solution and
665 prevented from engaging in further chemical reactions. This mechanism is
666 exacerbated in humus-rich peat soils, as organic matter has been found to prevent
667 the oxidative release of metals from other compounds (Hursthouse 2001). In
668 addition, acid pH conditions increase negative charges on organic soil particles,
669 more strongly retaining cations through sorption mechanisms and ligand exchange
670 (ATSDR 2005; Hursthouse 2001; Sparks 1995). This allows peat soils to
671 potentially act as a sink for storing more bioaccessible ionic forms of potentially
672 toxic elements.

673

674 Both Ni and Zn exhibit higher bioaccessibility in the presence of organic matter
675 and are also actively mobilised under acid conditions (EA 2009a; Nathanail et al.
676 2009; Poggio et al. 2009; Imrie et al. 2008), although less information is available
677 to clarify such trends for V. Nathanail et al. (2009) note that, unlike Zn and Ni,
678 acid pH generally immobilises V in soil solution, although this trend could not be
679 inferred from the data presented in this study. Previous mapping of the relative
680 spatial distributions of Ni, V and Zn did not reveal higher trace element
681 concentrations in areas of upland peat, but were instead spatially controlled by
682 local geologic formations, particularly where basalt bedrock was present (Barsby
683 et al. 2012). This, combined with the spatial illustration and correlations found
684 with chemical parameters associated with peat soil types, suggests that total trace
685 element concentrations are not necessarily an indication of the actual health risk
686 present from toxic metal exposure. It can additionally be inferred that Ni, V and
687 Zn bioaccessibility is likely to be elevated in peat soil types. Due to the precise
688 geographic correlation of SOC and SO₃ with peat soil across Northern Ireland and
689 the associated positive statistical correlations between SOC, SO₃ and trace
690 element bioaccessible fractions, it is concluded that peat soil types provide the
691 environmental conditions required to increase trace element mobility and

692 bioaccessibility including acidic pH, high chemical reduction potential, elevated
693 soil moisture and the presence of dissolved organic matter.

694

695 5. Conclusions

696

697 The strengthening of correlation statistics after division of BAF results into
698 generic geologic sub-groups suggests that substantial variance is introduced into a
699 data set when geochemistry is regarded collectively across a variety of rock
700 formations. Such grouping decreases this variance and allows the influence of
701 geology over trace element bioaccessibility to be more clearly exemplified.
702 Strong correlation statistics observed for the Antrim Basalts in particular suggest a
703 majority of variance in geochemistry and bioaccessibility is accounted for by the
704 local geology. Fewer statistically significant correlations in the other bedrock
705 groups indicate a higher degree of pedological or geogenic heterogeneity exists in
706 these areas, producing more variability in the results.

707

708 While relationships between the bioaccessible fractions of Ni, V and Zn and other
709 variables have been explored through correlation analysis and limited mapping
710 techniques, a more detailed presentation of the landscape scale processes driving
711 these relationships would further compliment this research. In addition, analysing
712 UBM data in groups according to rock types that are more specific than the
713 generic Tellus bedrock classifications may give clearer indications of geologic
714 influences over trace element bioaccessibility and help further reduce variance in
715 the data sets.

716

717 Geochemical mapping combined with correlation analysis in this study shows that
718 Ni, V and Zn bioaccessibility is anticipated to be higher in peat soil types in
719 Northern Ireland and is not necessarily a function of total trace element
720 concentrations, which is the factor dominating the contaminated land risk
721 assessment regulatory regime in the United Kingdom.

722

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980 analyses of geochemical variables of soils in Ireland. *Geoderma*, 146, 378-390.

Table 1 Summary statistics for BAF (%) results (from Barsby et al. 2012), total Ni, V, Zn (mg kg⁻¹) and oxide (%) concentrations

	Min	Max	Mean	St.Dev.	Min	Max	Mean	St.Dev.
Northern Ireland, n = 6862					Basalt Bedrock Group, n = 23			
Ni	1.40	333.60	46.21	48.65	4.90	185.30	77.66	59.65
V	5.90	401.60	99.66	65.04	18.10	280.00	157.88	88.98
Zn	2.80	2460.50	78.35	54.29	21.40	175.70	85.78	48.11
MgO	0.50	5.80	1.45	0.66	0.60	3.70	1.72	0.82
Al ₂ O ₃	3.50	17.20	10.61	2.98	4.00	14.90	10.59	3.37
SiO ₂	13.80	87.90	49.56	15.00	16.20	75.10	41.36	14.68
P ₂ O ₅	0.05	1.70	0.26	0.10	0.08	0.56	0.25	0.11
SO ₃	0.00	2.00	0.18	0.24	0.00	0.80	0.27	0.24
CaO	0.30	16.33	1.15	0.78	0.41	3.10	1.66	0.72
MnO	0.00	15.00	0.08	0.26	0.00	0.27	0.10	0.08
Fe ₂ O ₃	0.30	42.25	4.65	2.85	1.26	11.42	6.26	3.34
Lithic Arenite Bedrock Group, n = 17					Mudstone Bedrock Group, n = 18			
Ni	21.20	72.80	41.64	14.09	13.80	153.20	47.25	38.50
V	74.50	124.30	95.55	14.46	36.40	234.10	90.82	53.46
Zn	73.80	2460.50	242.25	572.48	41.70	151.90	83.85	33.23
MgO	1.10	2.80	1.71	0.40	0.70	2.60	1.40	0.54
Al ₂ O ₃	10.10	13.50	11.78	1.12	4.90	13.40	9.94	2.32
SiO ₂	41.10	67.60	56.84	7.80	19.60	73.30	51.09	13.09
P ₂ O ₅	0.15	0.48	0.31	0.09	0.18	0.55	0.28	0.09
SO ₃	0.00	0.80	0.11	0.21	0.00	0.80	0.23	0.30
CaO	0.53	2.08	0.83	0.39	0.56	3.64	1.52	0.95
MnO	0.04	0.19	0.08	0.04	0.03	0.27	0.09	0.06
Fe ₂ O ₃	2.96	6.31	4.37	0.85	1.76	10.21	4.40	2.20
Bioaccessibility Study Sample Set, n = 91					Basalt Bedrock Group			
V-G	1.92	22.50	8.72	4.59	3.82	22.50	11.19	5.65
V-GI	0.56	14.66	3.98	2.54	0.57	9.94	4.37	2.59
Ni-G	1.42	43.82	12.16	9.59	1.42	43.82	12.32	12.12
Ni-GI	0.60	14.45	5.50	2.92	0.60	9.98	4.49	2.66
Zn-G	4.28	80.76	22.17	17.63	6.92	80.76	26.85	22.42
Zn-GI	2.47	40.28	13.25	7.86	2.91	40.28	13.43	10.13
Lithic Arenite Bedrock Group					Mudstone Bedrock Group			
V-G	2.64	16.67	7.18	4.12	2.49	21.96	9.25	4.83
V-GI	0.95	8.35	3.33	2.20	1.25	14.66	4.94	3.46
Ni-G	3.01	42.17	9.87	9.77	4.13	33.62	14.50	8.71
Ni-GI	1.27	14.45	4.31	2.88	2.65	12.07	7.06	2.63
Zn-G	4.28	57.79	15.27	12.79	10.17	68.63	22.34	15.82
Zn-GI	2.47	16.45	7.62	3.37	4.98	24.06	13.34	5.50

Table 2 Pearson's Correlation Coefficients for Selected Geochemical Parameters and UBM Results (UBM data from Barsby et al. 2012)

	Total V	Total Ni	Total Zn	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	CaO	MnO	Fe ₂ O ₃	pH	SOC ²
Bioaccessibility Study Sample Set													
V-G	-.164	-.171	.127	-.331**	-.556**	-.379**	-.178	.542**	.121	-.414**	-.353**	-.143	.517**
V-GI	-.288**	-.305**	.125	-.413**	-.530**	-.134	-.029	.395**	.078	-.448**	-.473**	.022	.294**
Ni-G	-.447**	-.293**	.298**	-.511**	-.696**	-.536**	-.163	.754**	.006	-.396**	-.484**	-.310**	.723**
Ni-GI	-.511**	-.366**	.296**	-.543**	-.516**	-.102	-.080	.428**	-.090	-.355**	-.531**	-.057	.269**
Zn-G	-.433**	-.291**	.182	-.479**	-.805**	-.605**	-.177	.727**	.124	-.389**	-.462**	-.294**	.810**
Zn-GI	-.582**	-.550**	-.071	-.661**	-.707**	-.207*	-.331**	.376**	-.199	-.586**	-.619**	-.325**	.446**
Basalt Bedrock Group													
V-G	-.533**	-.606**	-.638**	-.612**	-.679**	-.410	-.581**	.606**	-.251	-.736**	-.690**	-.532**	.626**
V-GI	-.510*	-.696**	-.709**	-.676**	-.593**	-.138	-.547**	.394	-.355	-.766**	-.736**	-.473*	.406
Ni-G	-.749**	-.611**	-.682**	-.712**	-.826**	-.552**	-.563**	.677**	-.570**	-.651**	-.718**	-.696**	.811**
Ni-GI	-.784**	-.700**	-.757**	-.710**	-.607**	-.048	-.591**	.214	-.689**	-.695**	-.789**	-.426*	.390
Zn-G	-.761**	-.600**	-.676**	-.691**	-.890**	-.563**	-.588**	.724**	-.555**	-.649**	-.713**	-.743**	.854**
Zn-GI	-.828**	-.751**	-.834**	-.824**	-.828**	-.222	-.655**	.451*	-.762**	-.763**	-.833**	-.685**	.605**
Lithic Arenite Bedrock Group													
V-G	-.121	-.018	-.140	-.294	-.723**	-.493*	.054	.775**	.083	-.431	-.591*	-.165	.641**
V-GI	-.231	-.104	-.177	-.334	-.673**	-.430	.170	.764**	.055	-.441	-.652**	-.133	.607**
Ni-G	-.329	-.251	-.148	-.322	-.552*	-.585*	-.309	.943**	-.217	-.306	-.510*	-.407	.806**
Ni-GI	-.345	-.261	-.150	-.398	-.543*	-.383	-.284	.892**	-.291	-.274	-.559*	-.328	.649**
Zn-G	-.381	-.327	-.237	-.324	-.567*	-.529*	-.119	.952**	-.193	-.213	-.529*	-.382	.756**
Zn-GI	-.527*	-.506*	-.412	-.358	-.556*	-.445	.087	.842**	.007	-.299	-.602*	-.076	.666**
Mudstone Bedrock Group													
V-G	-.299	-.196	-.182	-.501*	-.730**	-.145	.257	.421	.436	-.500*	-.435	.463	.387
V-GI	-.434	-.330	-.263	-.532*	-.827**	-.118	.308	.378	.415	-.505*	-.558*	.474*	.399
Ni-G	-.264	-.136	.010	-.456	-.652**	-.750**	.351	.925**	.724**	-.405	-.364	.121	.871**
Ni-GI	-.356	-.241	-.066	-.403	-.550*	-.360	.144	.719**	.432	-.381	-.449	.196	.501*
Zn-G	-.345	-.225	.034	-.360	-.753**	-.645**	.438	.637**	.756**	-.380	-.428	.393	.854**
Zn-GI	-.717**	-.658**	-.560*	-.607**	-.878**	-.131	.250	.304	.268	-.658**	-.834**	.358	.381

**Correlation is significant at the 0.01 level (2-tailed)

*Correlation is significant at the 0.05 level (2-tailed)

²As estimated by loss on ignition

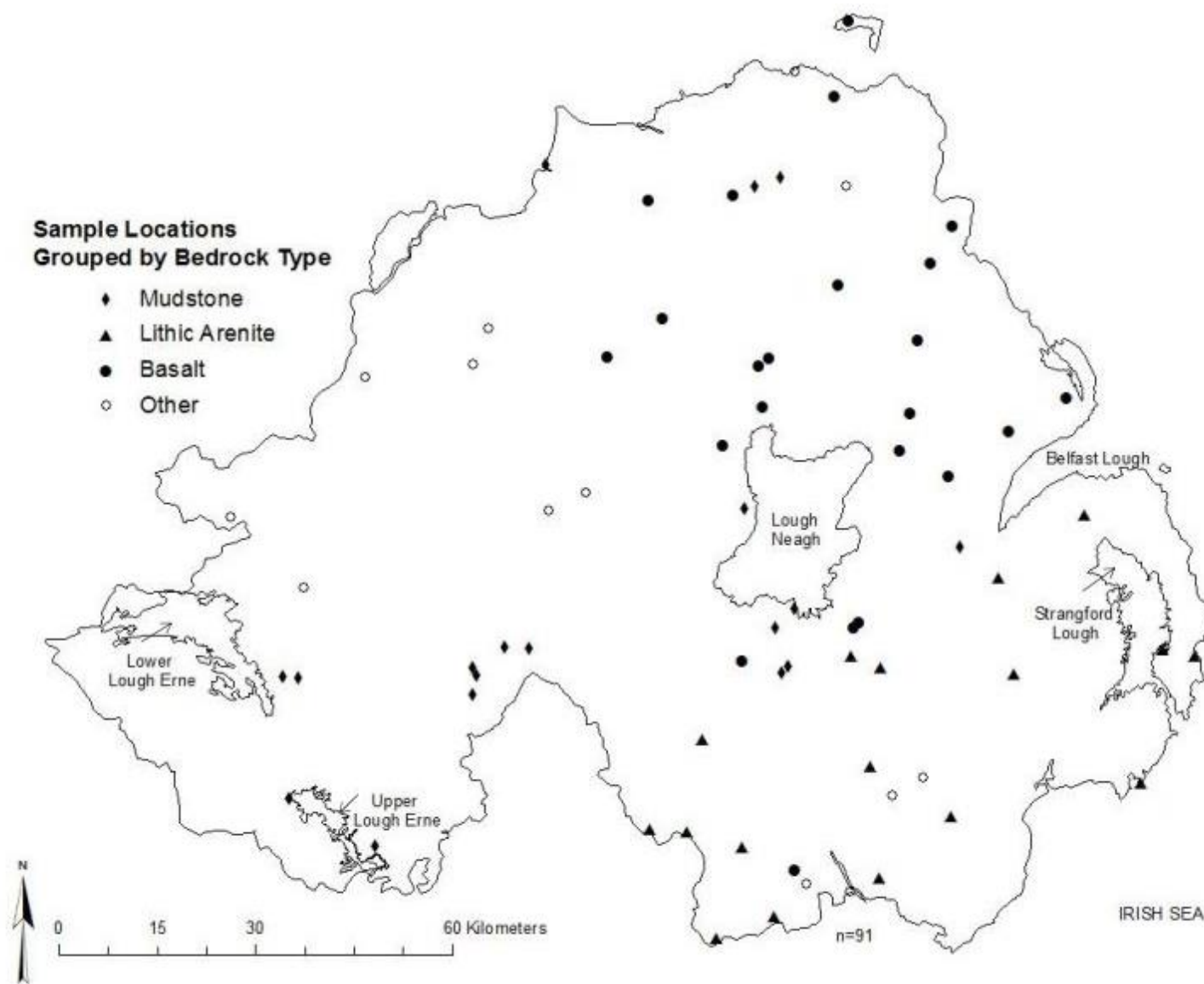


Fig. 1 Northern Ireland soil sample location map for bioaccessibility testing with bedrock classification

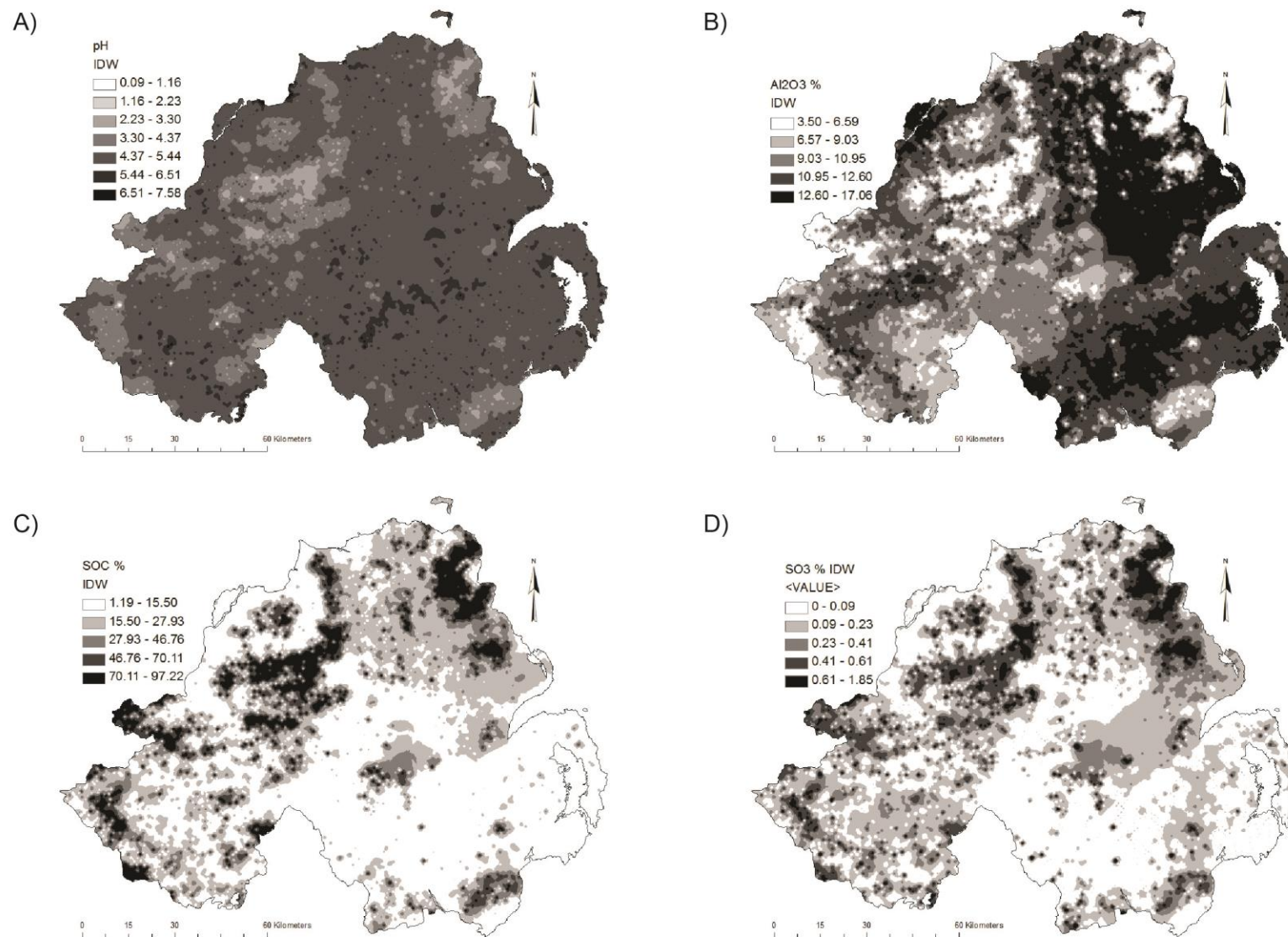


Fig. 2 pH, Al₂O₃, SO₃ and estimated SOC interpolated by IDW, 12 neighbours, showing highest and lowest proportional distributions and acidity in areas of upland peat deposits across Northern Ireland

Supporting Information:

Table A. Skewness and kurtosis values for Ni, V and Zn, demonstrating a general increase towards a normal distribution after bedrock group sub-division

	Skewness	Kurtosis
V N. Ireland	1.00	0.50
V Study Set	1.18	0.56
V Basalt	-0.24	-1.43
V Lithic Arenite	0.29	-0.57
V Mudstone	1.30	1.5
Ni N. Ireland	1.89	3.66
Ni Study Set	1.98	4.01
Ni Basalt	0.57	-0.90
Ni Lithic Arenite	0.67	-0.15
Ni Mudstone	1.20	0.12
Zn N. Ireland	14.28	556.89
Zn Study Set	8.97	83.44
Zn Basalt	0.27	-1.02
Zn Lithic Arenite	1.60	2.50
Zn Mudstone	0.73	-0.44

N. Ireland values, n = 6862; study set, n = 91; basalt, n = 23; lithic arenite, n = 17; mudstone, n = 18